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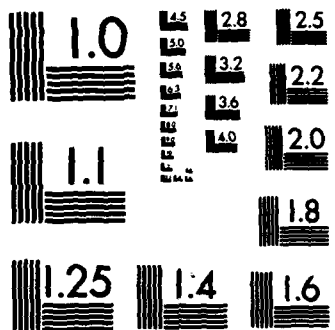
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ELECTRICALLY CONDUCTING POLY(VINYL ACETATE)

by

John J. Fontanella & Mary C. Wintersgill

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INTRODUCTION

Electrically conducting polymers have recently been the subject of intense interest. Polyacetylene has been widely studied as an electronic conductor. Ionic conductors include poly(ethylene oxide) (1), poly(propylene oxide) (2), polyacrylonitrile (3), poly(vinylidene fluoride) (3), poly(tetramethylene oxide) (4) and poly(ethylene succinate) (5). In the present note, the observation of electrically conducting poly(vinyl acetate) (PVAc) is reported. Ionic conduction is inferred from the data.

EXPERIMENT AND RESULTS

PVAc (MW 1.5×10^6) was obtained from Polysciences, Inc. PVAc and LiClO_4 in the ratio 8:1 were dissolved in methanol then dried in air on a teflon plate at about 55°C . The result was a brittle, clear solid at room temperature. Pure PVAc was prepared by the same method for comparison. Aluminum electrodes were then evaporated onto the faces of several samples and audio frequency complex impedance measurements were performed in a vacuum at temperatures from 5.5 K to 380 K using techniques described elsewhere (6). The results for one frequency (100 Hz) are shown in figure 1. Four other frequencies from $100\text{--}10^4$ Hz gave similar results and are omitted for clarity. It is seen that the d.c. conductivity of the LiClO_4 complexed material at 100°C is about three orders of magnitude larger than that of the pure material and increases exponentially with an activation energy of about 2.1 eV. However, at about 50°C the a.c. conductivity of the pure material (a.c. loss due to the relaxation peak associated with the glass transition) is slightly greater than that for the complexed material at the same temperature. The glass

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Key words: polymer electrolytes
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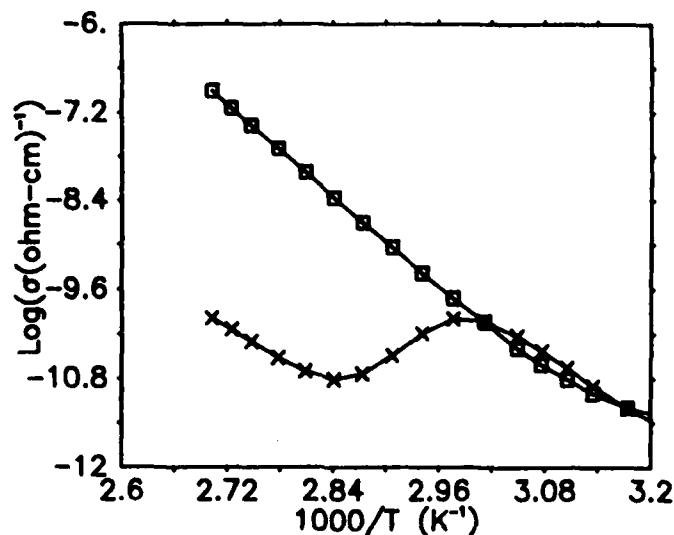


Fig. 1. $\text{Log}(\sigma(\text{ohm-cm})^{-1})$ vs. $1000/T$ (K^{-1}) for pure PVAc (x) and PVAcg-LiClO₄ (□) at 100 Hz.

transition in the complexed material is shifted to higher temperatures where it is probably masked by the d.c. conductivity. This temperature shift is confirmed by differential scanning calorimetry (DSC) studies. The DSC results together with further electrical relaxation studies will be presented elsewhere.

In order to gain further information concerning this material, ⁷Li NMR linewidth and spin-lattice relaxation T_1 measurements were conducted at 155 MHz with a JEOL GX400 NMR spectrometer, after sealing the sample in an evacuated quartz tube. Over the temperature range studied, the ⁷Li spectra exhibit a single absorption with no apparent quadrupolar broadening (as deduced by the appropriate $\pi/2$ pulsedwidth condition). The temperature dependence of the full-width-at-half-maximum (FWHM)-linewidth is shown in figure 2 (triangles). The T_1 -recovery process was found to be slightly non-exponential, which may indicate the presence of more than one relaxation time. However, no significant temperature dependence of the recovery profile was observed, which allowed the use of an "effective T_1 ," defined as the time required

for the magnetization to recover 63% of its maximum value. A plot of T_1 (effective) vs. $1000/T$ also appears in Figure 2 (squares). The value of the "rigid linewidth" (4.4 kHz), which occurs below about 220K and the observed motional narrowing behavior bear a close similarity to results reported for PEO-Li⁺-based materials,^{7,8} which suggests a comparable degree of Li⁺ and/or polymer chain motion in PVAcg-LiClO₄. There are, unfortunately, no T_1 measurements above 383K at present, but it is likely that a T_1 minimum would occur at or near the melting point of the complex. T_1 does, however, exhibit Arrhenius behavior throughout the motional narrowing region (above room temperature) with an activation energy of 0.14 ± 0.03 eV. This small value presumably reflects localized motion with a correspondingly small potential energy barrier. The relation between the apparent localized process and motion resulting in long-range transport is not clear at the present time.

Finally, the following cell was constructed: Li/PVAcg-LiClO₄/MnO₂-C-PVF₂. The composition of the cathode was about 82% MnO₂, 9.6% C and 8.4% PVF₂ by weight. The materials were hot-pressed at about 205°C to form a conducting disk about 2.54 cm in diameter and 1 mm thick. The polymer film was about 0.4 mm thick and 2 cm in diameter, while the lithium electrode was about 1 mm thick with a diameter of about 1.2 cm. The three disks were spring loaded into a cell under an argon atmosphere. The cell was not hermetically sealed. Although the present data were obtained with the cell in air, similar results were obtained when the experiment was carried out under vacuum. The discharge characteristics are shown in figure

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3. Further tests showed that with a $100\text{k}\Omega$ load, the voltage decreased gradually from 1.8V to 0.9V over a period of 16 hours. The cell failed at that time. While the discharge characteristics of the present cell are not particularly impressive, it should be emphasized that no attempt was made to optimize the performance of the cell. The construction of the cell was rather primitive and, for example, a higher operating temperature or thinner polymer would decrease the internal resistance of the cell. The "open circuit" voltage (the resistance of the Keithley 195 DMM is about 10^6 ohms) is about 3.04 volts, which is not unreasonable for a cell of this type. Further, the initial internal resistance of the cell, was about $93\text{k}\Omega$ and was about 85 times larger than the resistance predicted from the a.c. conductivity measurements described above. While there is considerable uncertainty in the latter value due to the ambiguities in the geometry of the cell, it is clear that the internal resistance of the cell is larger than the a.c. resistance of the bulk polymer material. This is not surprising since, for example, anions as well as cations may be contributing to the a.c. conductivity, thus giving rise to a lower a.c. resistance. Finally, a similar cell was constructed using a pure PVAc film in place of the PVAcg-LiClO₄. No voltage was detected for this cell.

All results are consistent with ion transport.

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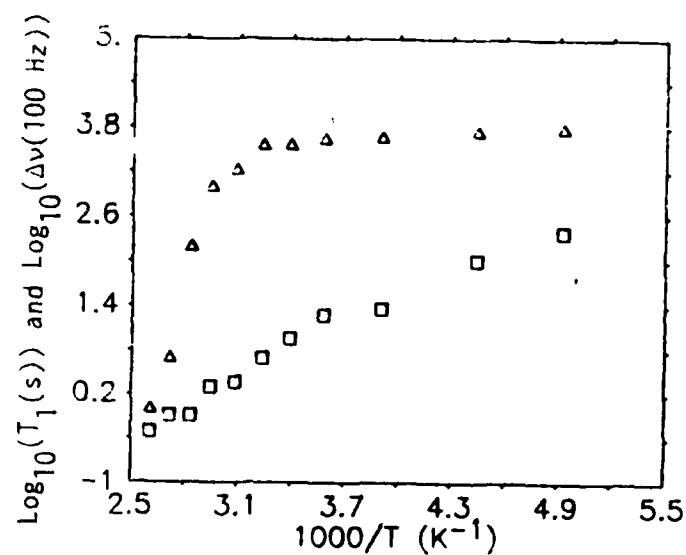


Fig. 2. Temperature dependences of ^7Li FWHM linewidth (Δ) and effective T_1 (\square).

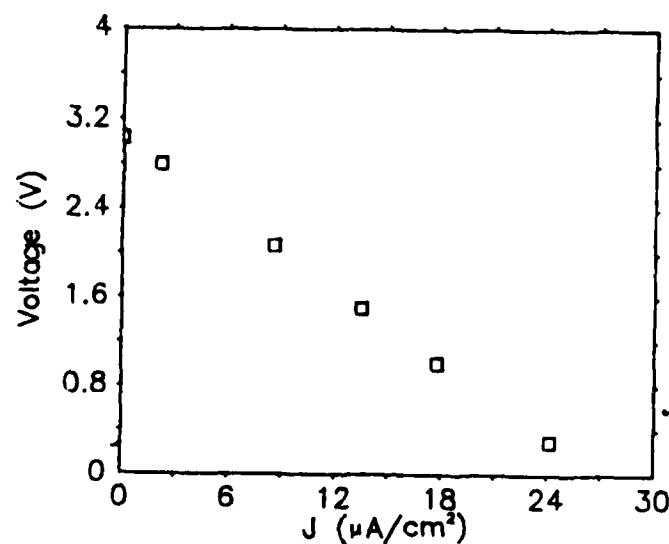


Fig. 3. Voltage (V) vs. $J(\mu\text{A/cm}^2)$ for the cell: $\text{Li/PVAcg-LiClO}_4/\text{MnO}_2\text{-C-PVF}_2$ at 125°C .

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